# Application of Biosorption for REE Recovery from Coal Byproducts

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U.S. DEPARTMENT OF ENERGY

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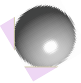
# Project Description and Objectives

## A selective adsorption process using bioengineered microbes

**Step 2:**

Rare earth biosorption




**Step 1:**

Bioengineer microbes

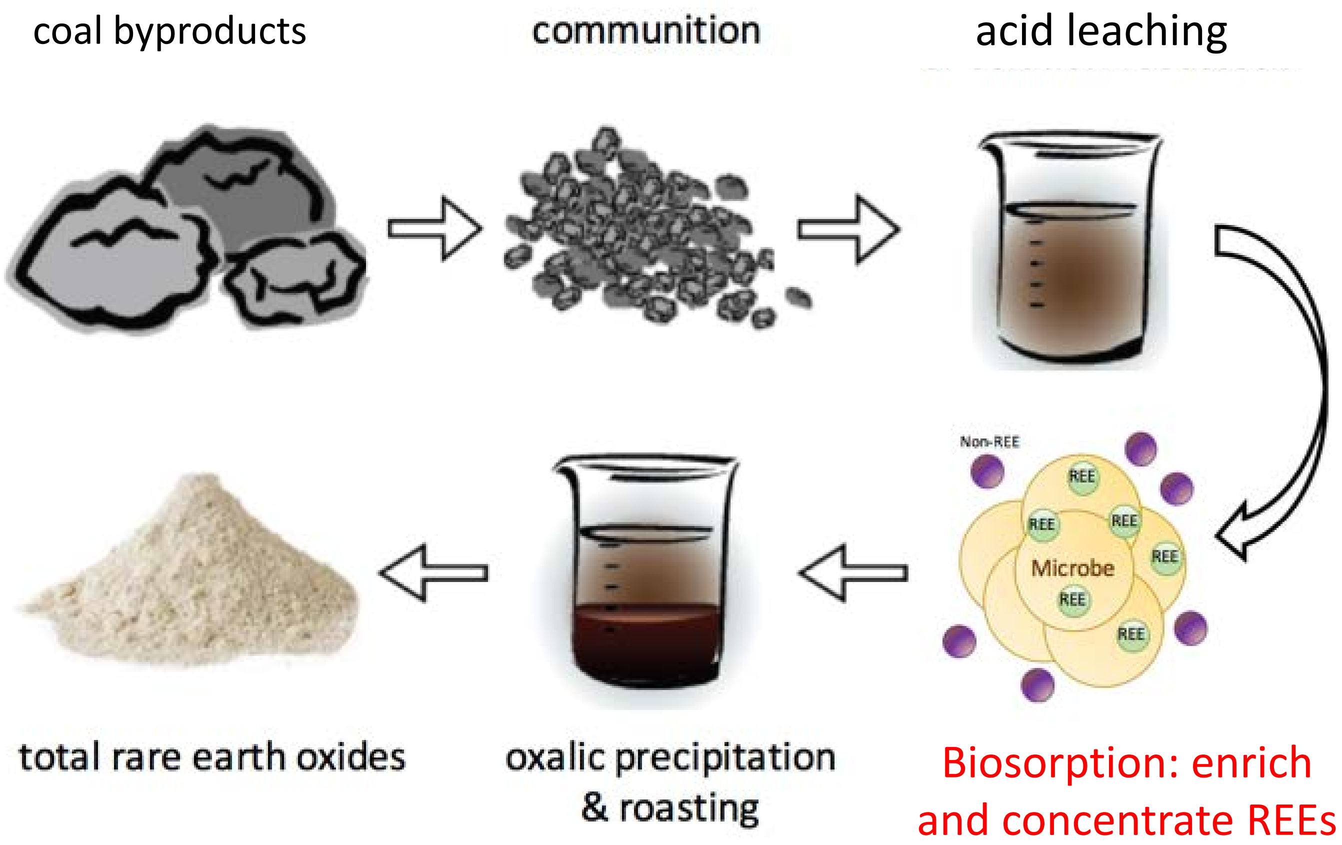
**Step 3:**

Rare earth recovery

Patent issued Feb 2019

# Project Description and Objectives

**Develop a cost-effective and environmentally sustainable biosorption technology for REE recovery from coal byproducts**



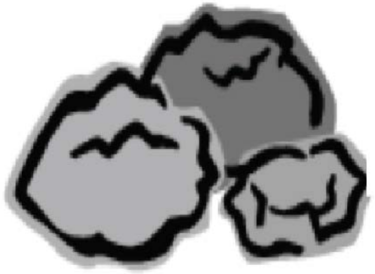
# Project Description and Objectives

## Develop Biosorption for REE Recovery from Coal Byproducts

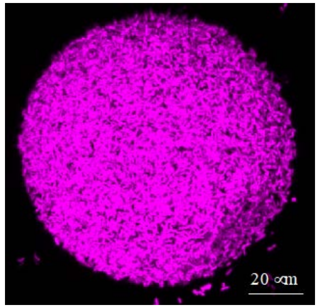
1. **Feedstock checklist** – Acid leaching of feedstocks and REE adsorption tests at batch scale.
    - **Pre-combustion coal byproducts:** lignite from ND and clays of coal bed floor from NM
    - **Fly ash:** from power plants burning coal from Central Appalachian and Powder River Basin
2. **Develop a flow-through system –** Microbe encapsulation and REE recovery in a packed bed bioreactor.
    - **Microbe bead synthesis:** developed a high-throughput microbe bead synthesis method.
    - **Column experiments:** REE adsorption was tested with mock solutions.
3. **Technical-economic analysis –** preliminary but informative
    - **Identify steps with high price tags:** acid leaching and polymer/oil for bead synthesis, and waste management
    - **Suggest solutions to lower cost:** increase adsorptive capacity and column reuse cycles, and explore alternative polymers.

# Project Description and Objectives

## Project highlights



Leaching
Duke U.




Microbe bead
LLNL


Column
LLNL

TEA
U. Arizona

- A graduate student and a postdoc supported at LLNL.
- Two graduate students supported at Duke U. and U. of Arizona.
- A U.S. patent issued Feb 2019.
- A user project supported by Environmental Molecular Sciences Laboratory (EMSL).

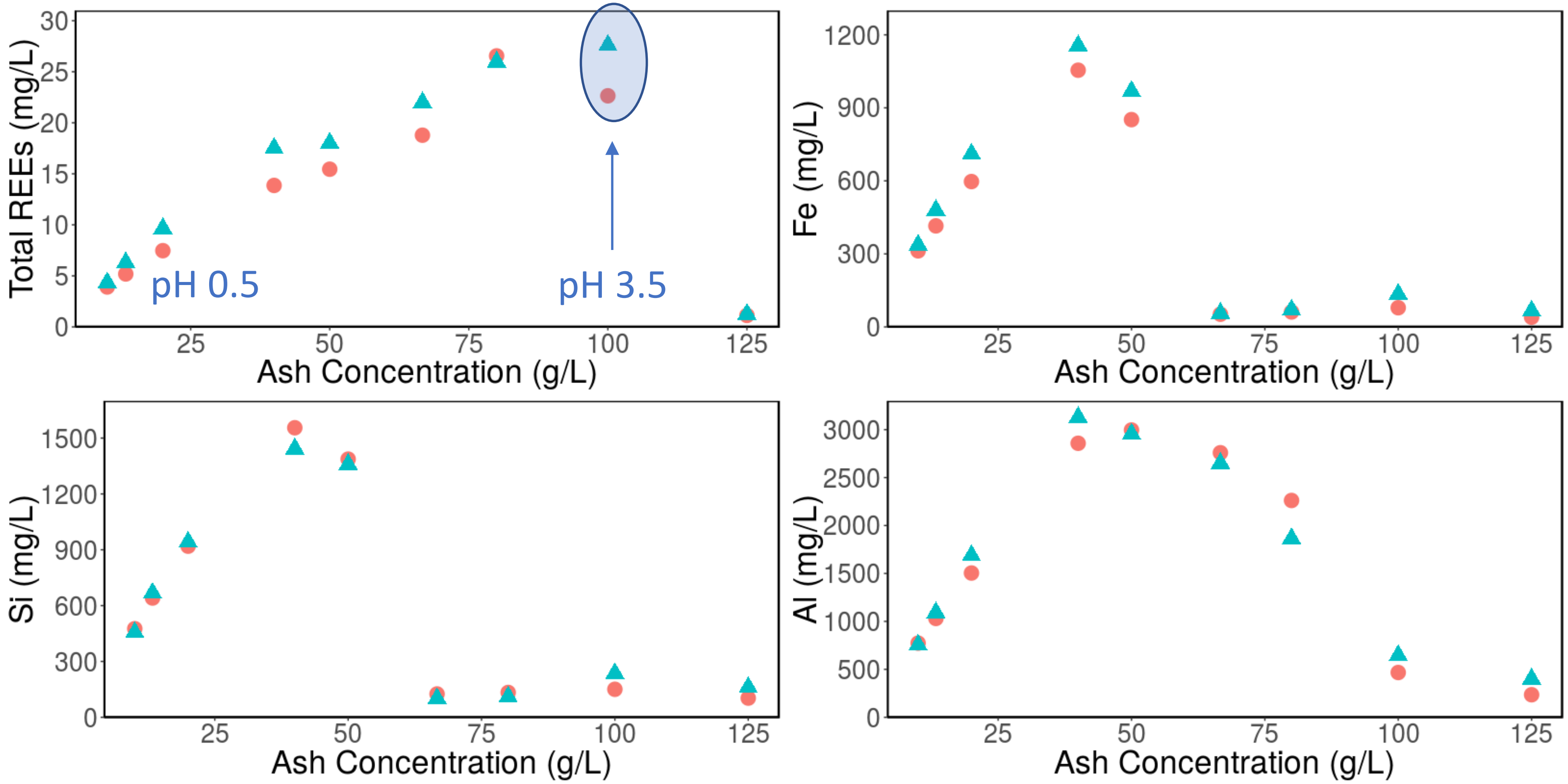
# Project Update

## Obtained and tested 4 feedstocks

| Feedstock type | Location | REE content (ppm) | Power plant information | Other notes |
|---|---|---|---|---|
| **Lignite** | North Dakoda | 100-600 | N/A | Dan Laudal,<br>DOI: 10.1016/j.coal.2018.03.010 |
| **Fly ash** | Power River Coal Basin | 300-400 | Texas, South Carolina power plant | Taggart et al |
| **Fly ash** | Central Appalachian coal basin | 500-700 | Kentucky, South Carolina power plants | Taggart et al<br>(DOI: 10.1021/acs.est.6b00085) |
| **Pre-combustion clays coal bed floor** | Navajo Indian Reservation in northern Arizona | 200 | N/A | Personal communication with Navajo Transitional Energy Company. |
| **Ion adsorption clay** | A surface mine, PA | 300-500 | N/A | Peter Rozelle et al<br>DOI: 10.1007/s40553-015-0064-7 |
| **Acid Mine Drainage** | Appalachian streams | Solution phase and sludge (100-300) | N/A | West Virginia |

# Project Update

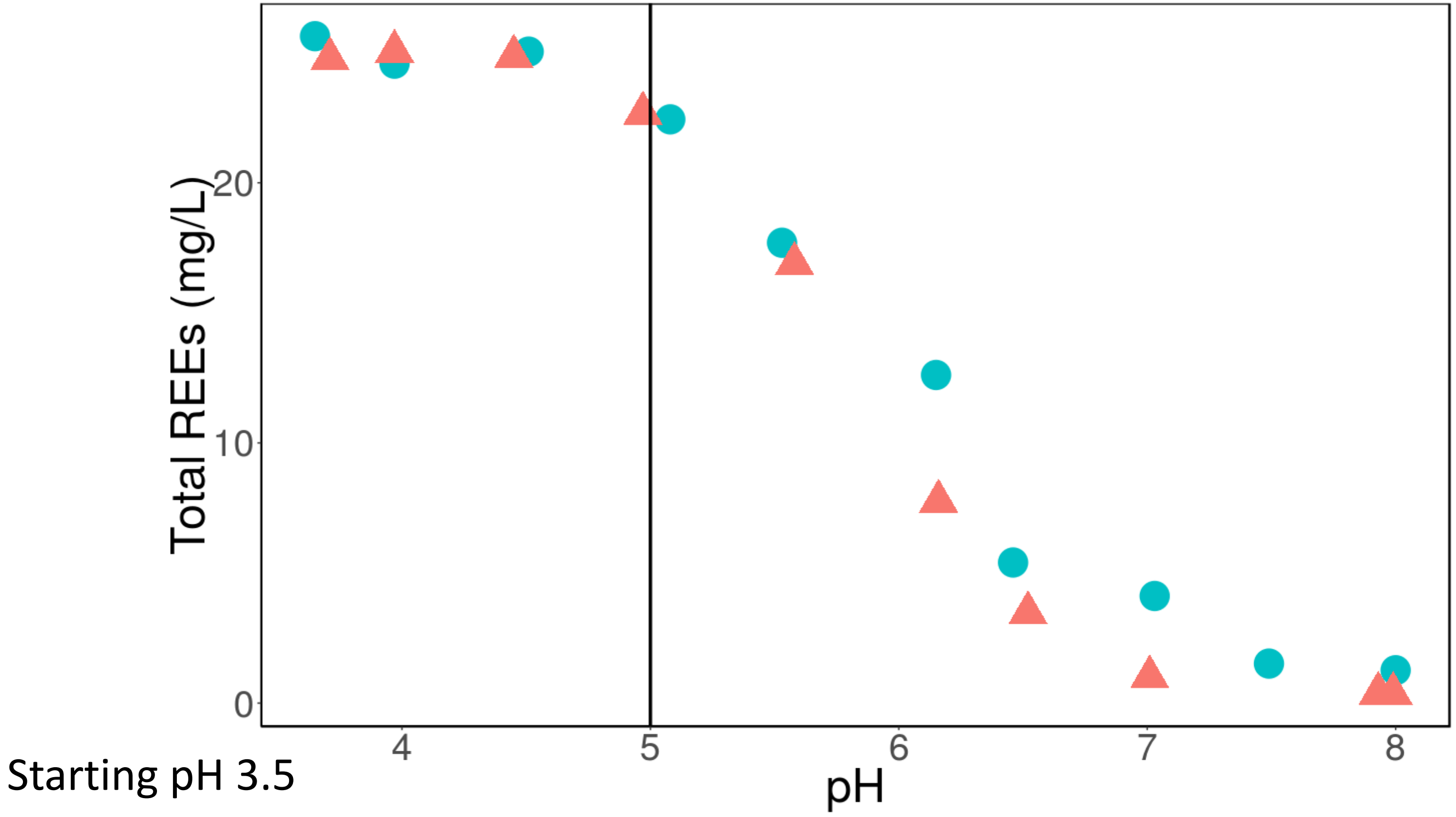
## Acid leaching of PRB fly ash at different solid: liquid ratios




1M HCl at 85℃.

# Project Update

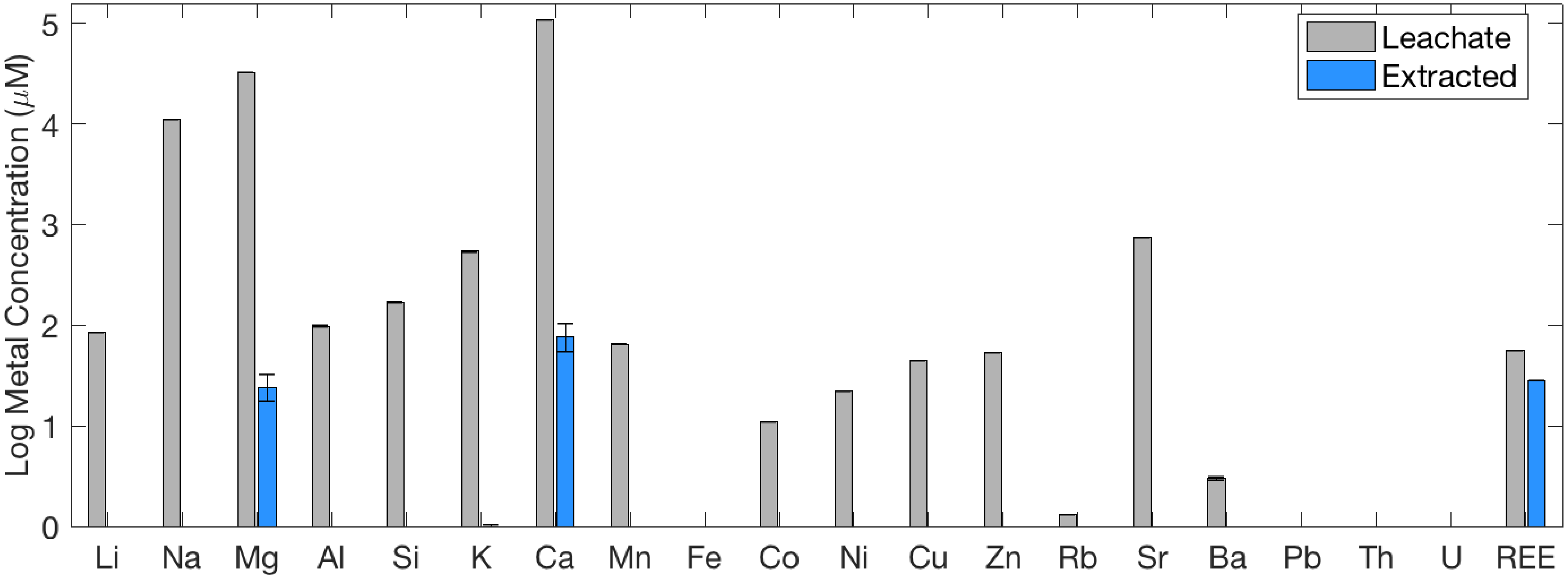
## REE solubility of PRB leachate upon pH adjustment




100 g/L ash

# Project Update

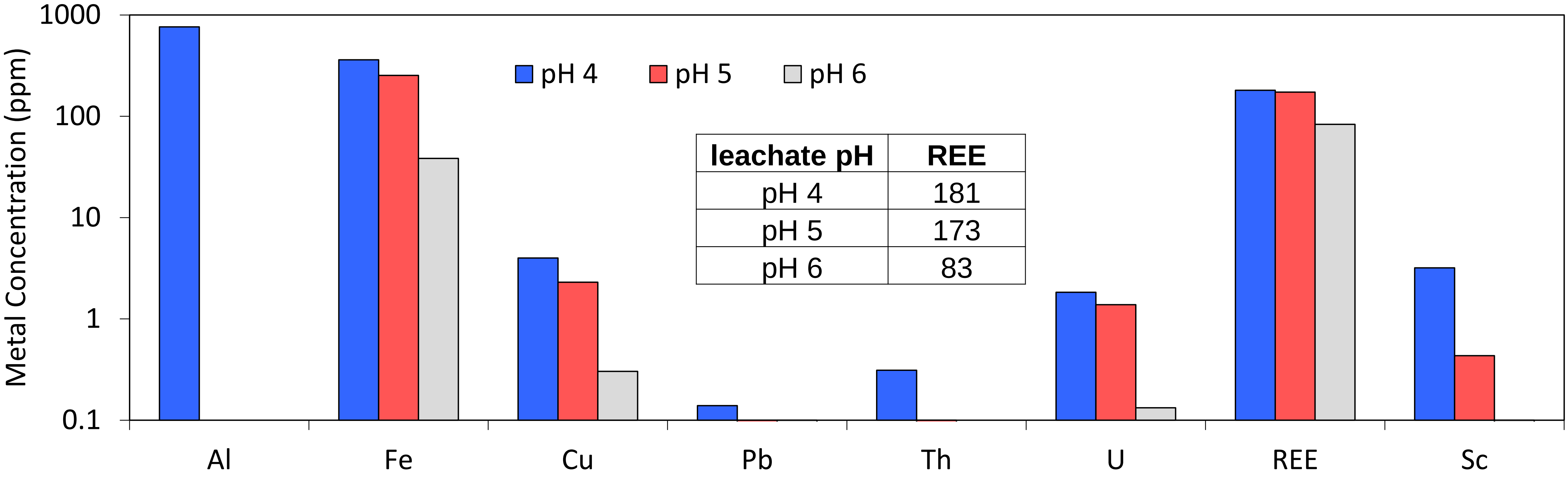
## Adsorption with PRB leachate at pH 5




Biosorption is highly selective towards REEs

# Project Update

## REE solubility of lignite leachate upon pH adjustment

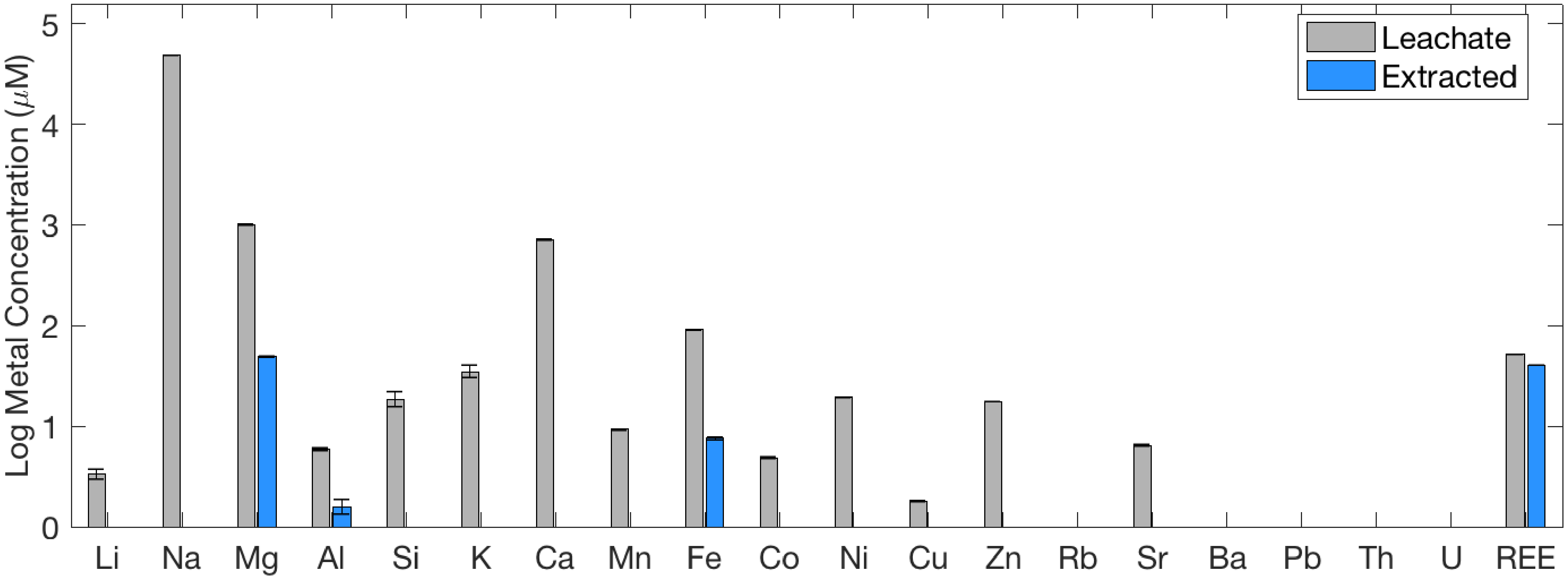



| leachate pH | REE |
|---|---|
| pH 4 | 181 |
| pH 5 | 173 |
| pH 6 | 83 |

- Lanthanides are soluble up to pH 5
- Sc is soluble only up to pH 4

# Project Update

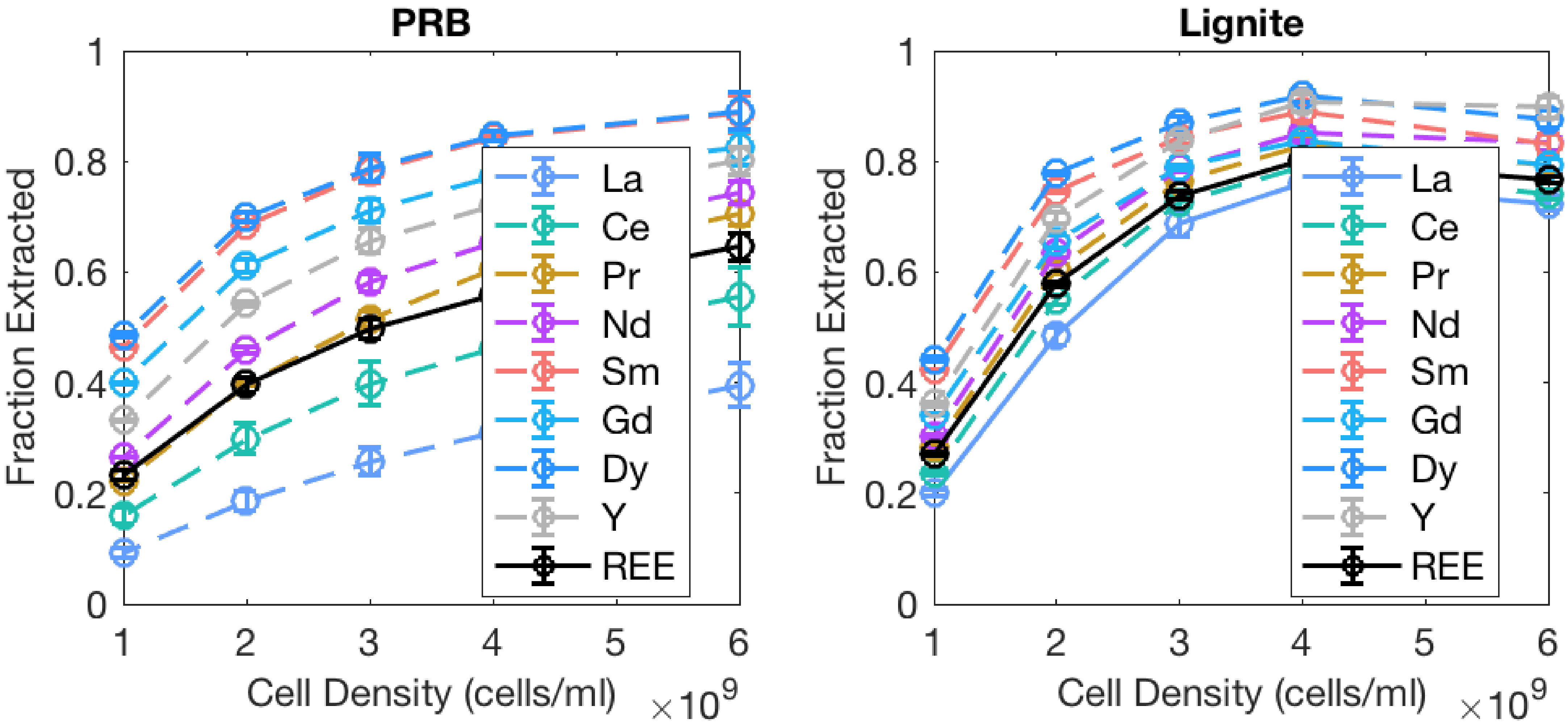
## REE biosorption from lignite leachate at pH 5




Biosorption is highly selective towards REEs

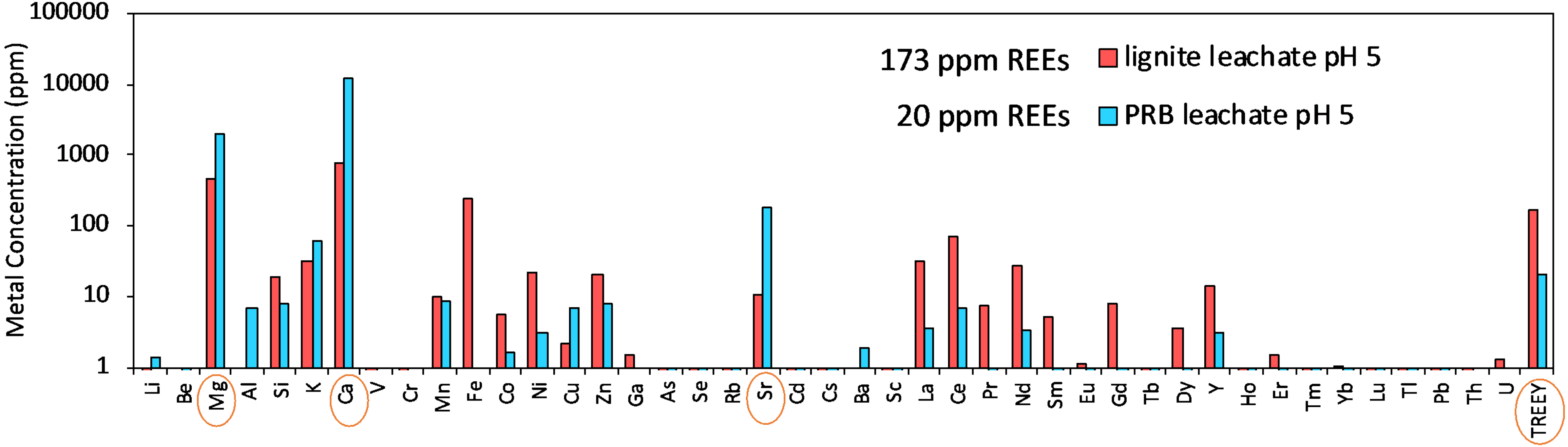
# Project Update

## REE recovery efficiency between PRB and lignite



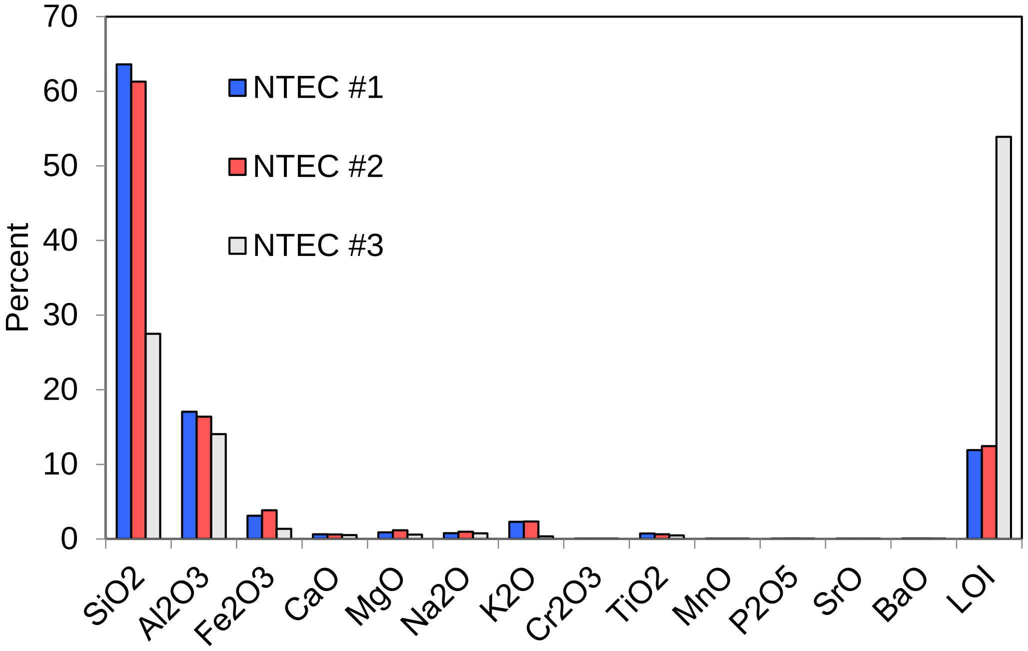
# Project Update

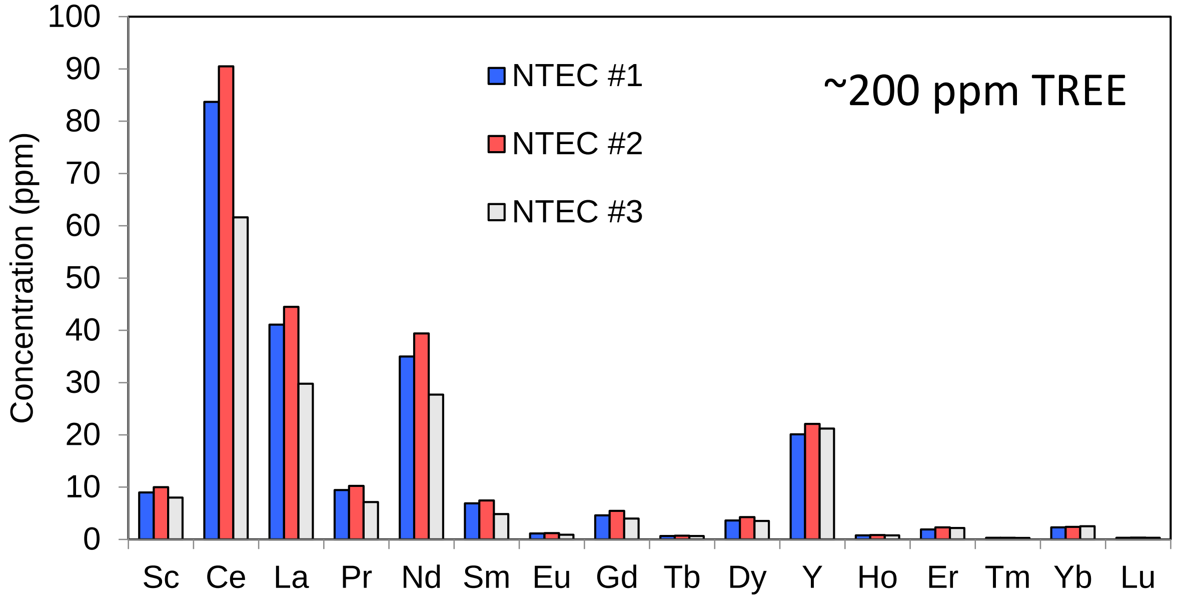
## Comparison of metal/REE composition between lignite and PRB



# Project Update

## Composition analysis of coal bed floor clays from Navajo (NM)




#1

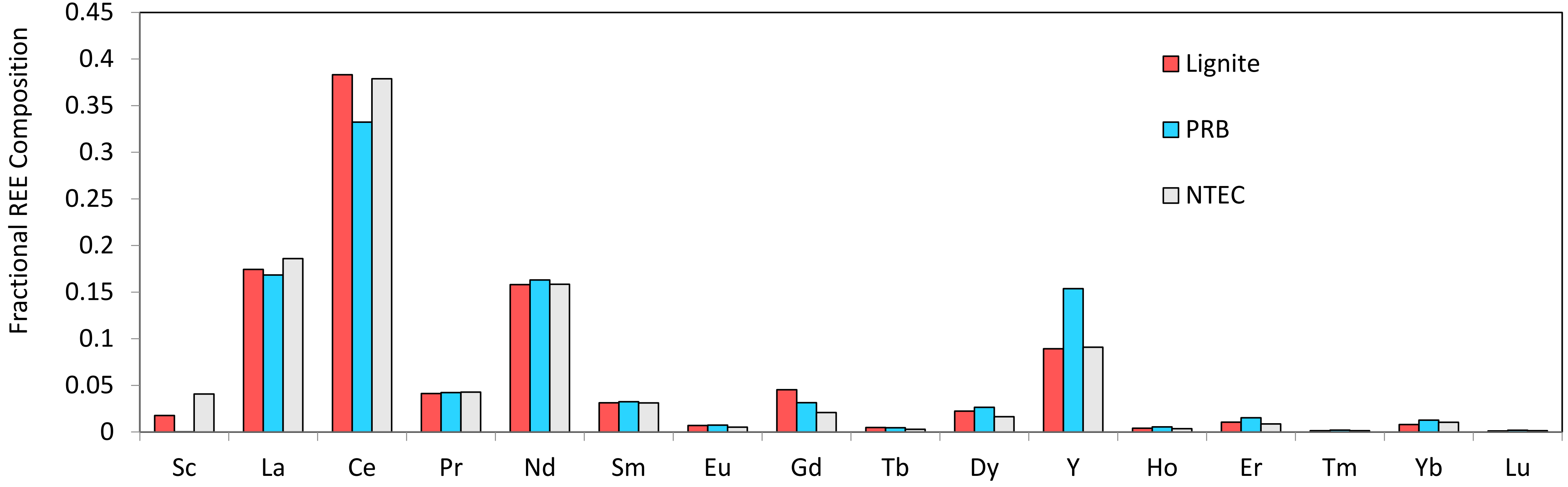
#2

#3

High LOI
High TOC?

# Project Update

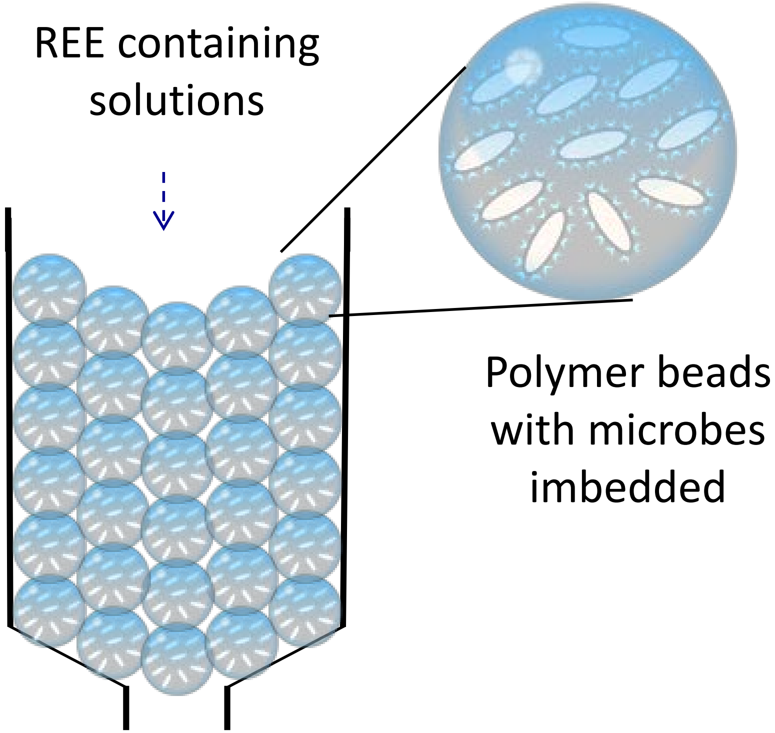
## REE composition of feedstocks




Similar REE composition profiles are observed for all three feedstocks.

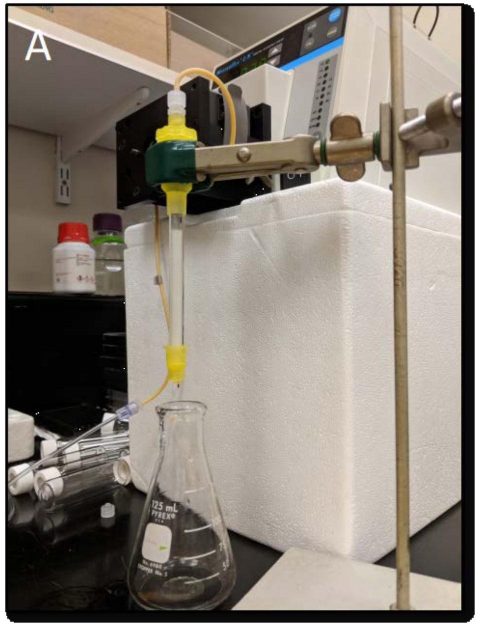
# Project Update

## Develop a continuous flow through system



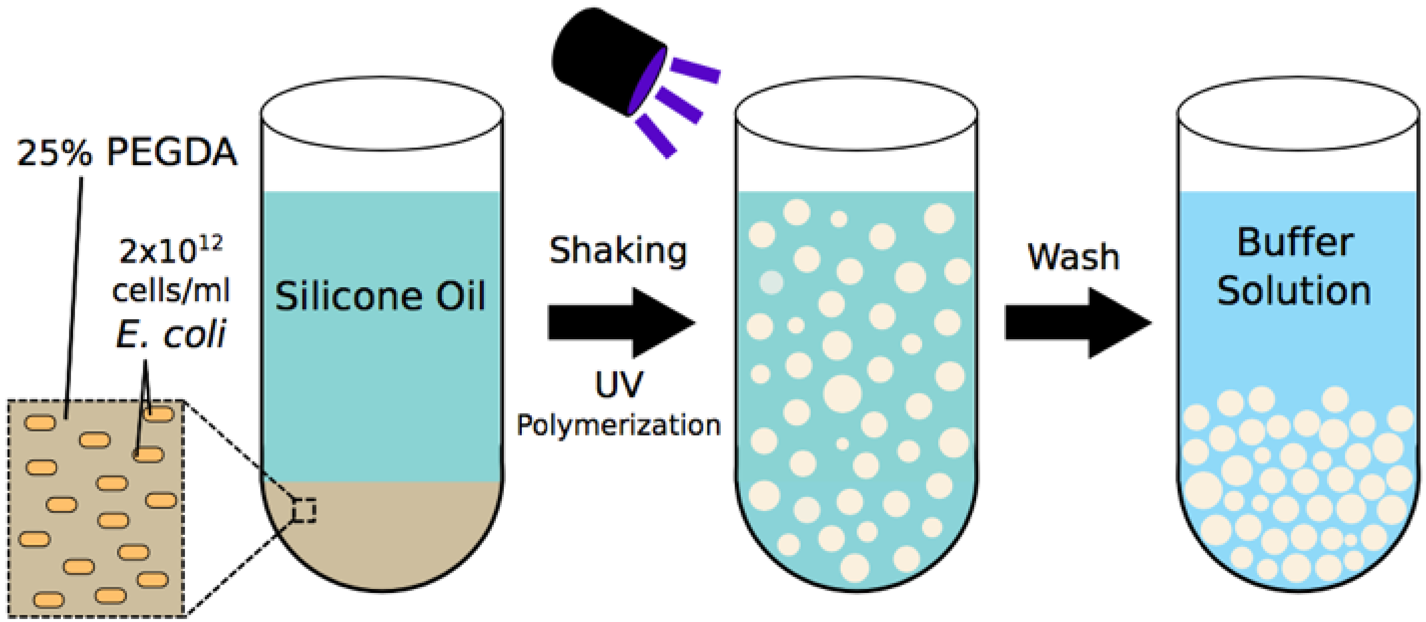

Cell encapsulation coupled with column chromatography

- Bioengineered REE-adsorbing microbes are embedded in hydrogel to make microbe beads
- Microbe beads are used as resin for columns



# Project Update

## A bulk emulsification method for microbe encapsulation

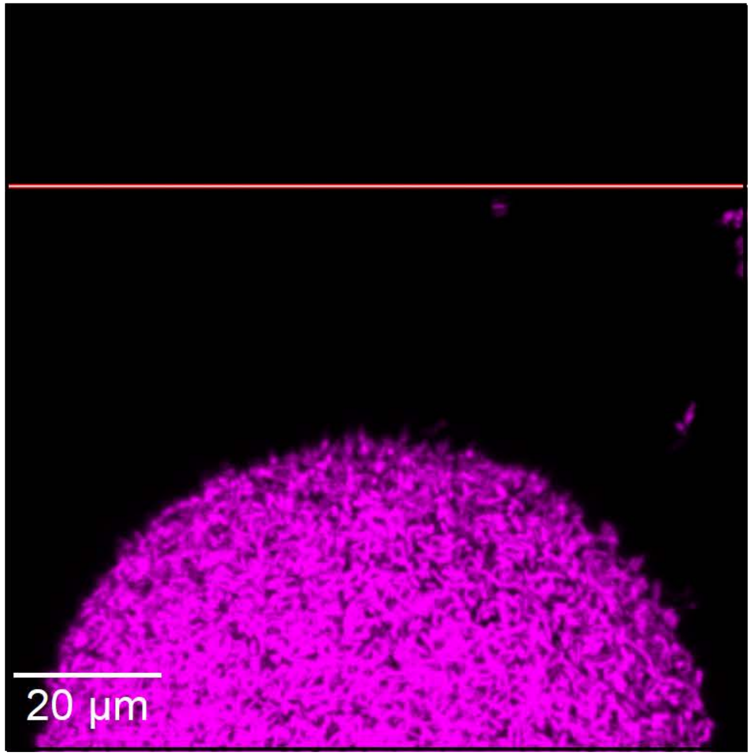


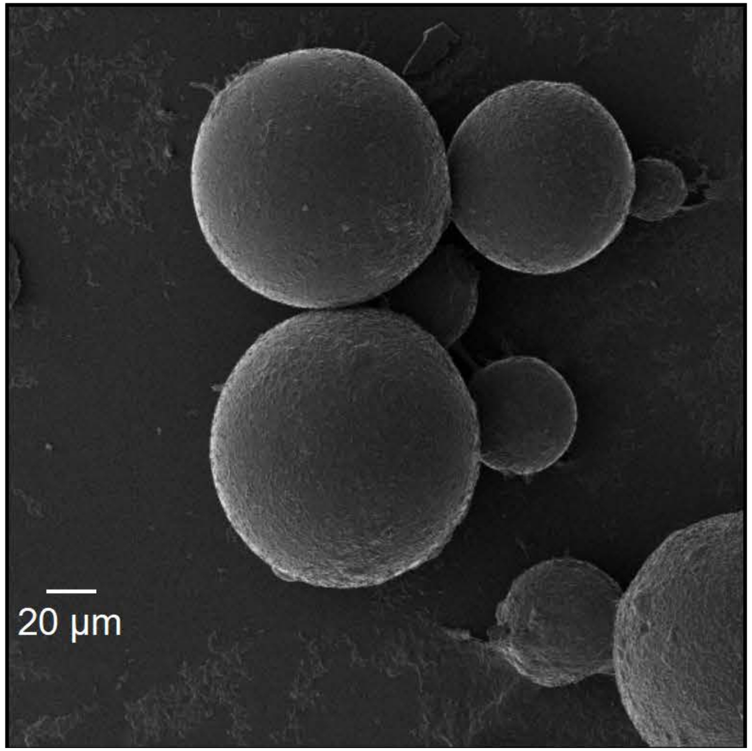

Compared to a microfluidic method used initially:

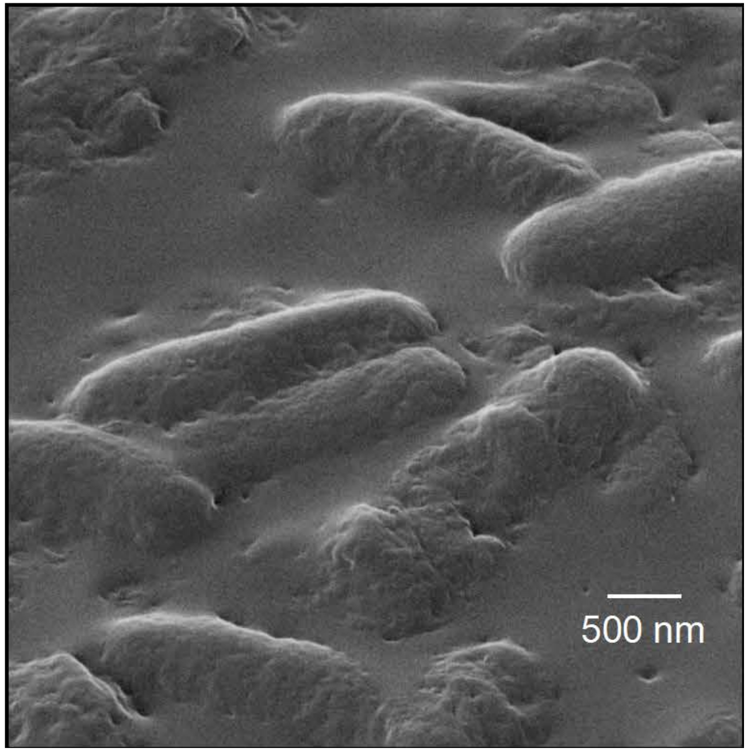
- Increased cell loading by 20-fold
- Increased bead synthesis throughput by 10-fold
- A scalable process

# Project Update

## Microbe bead synthesis and characterization

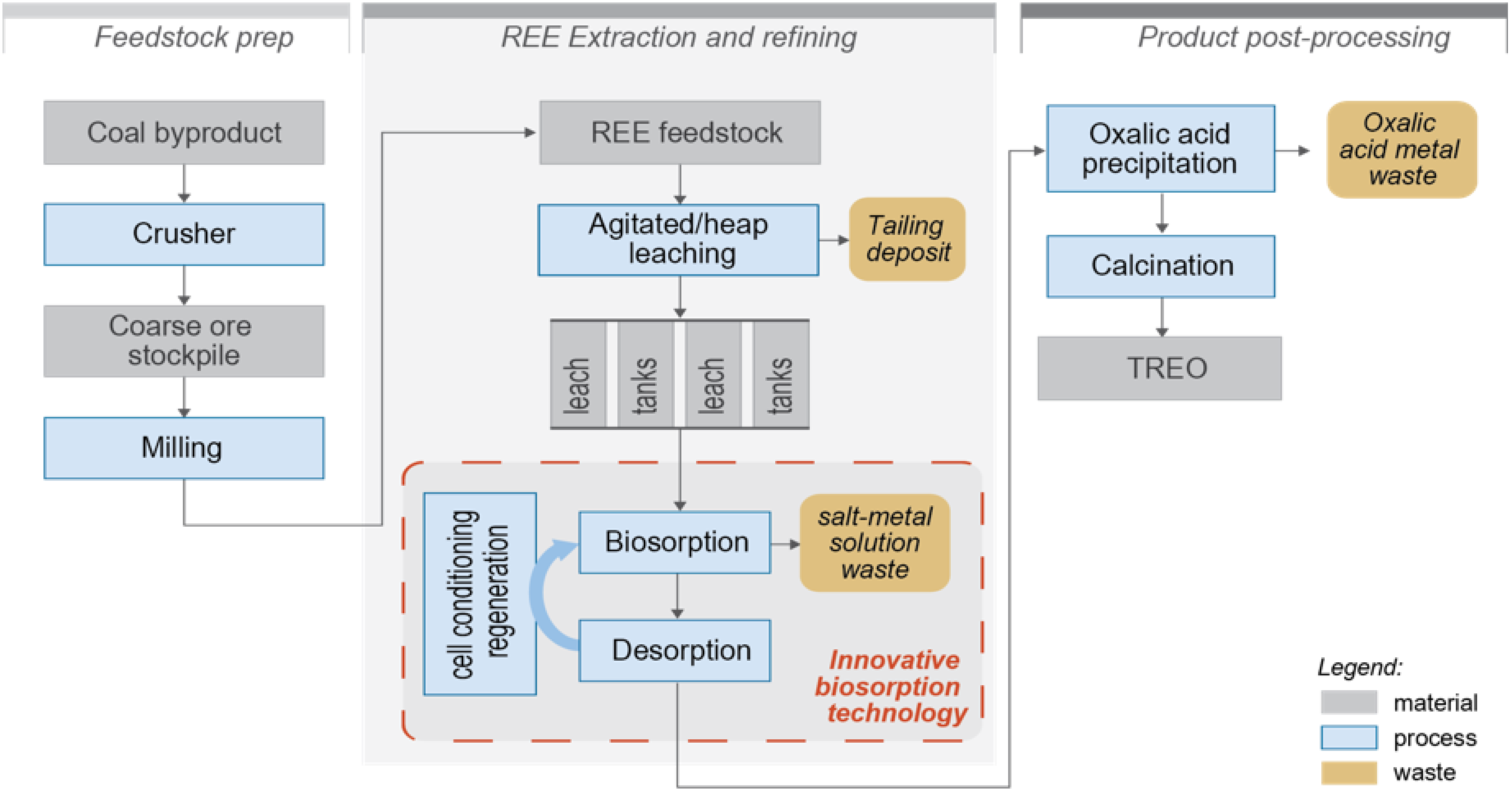


# Project Update

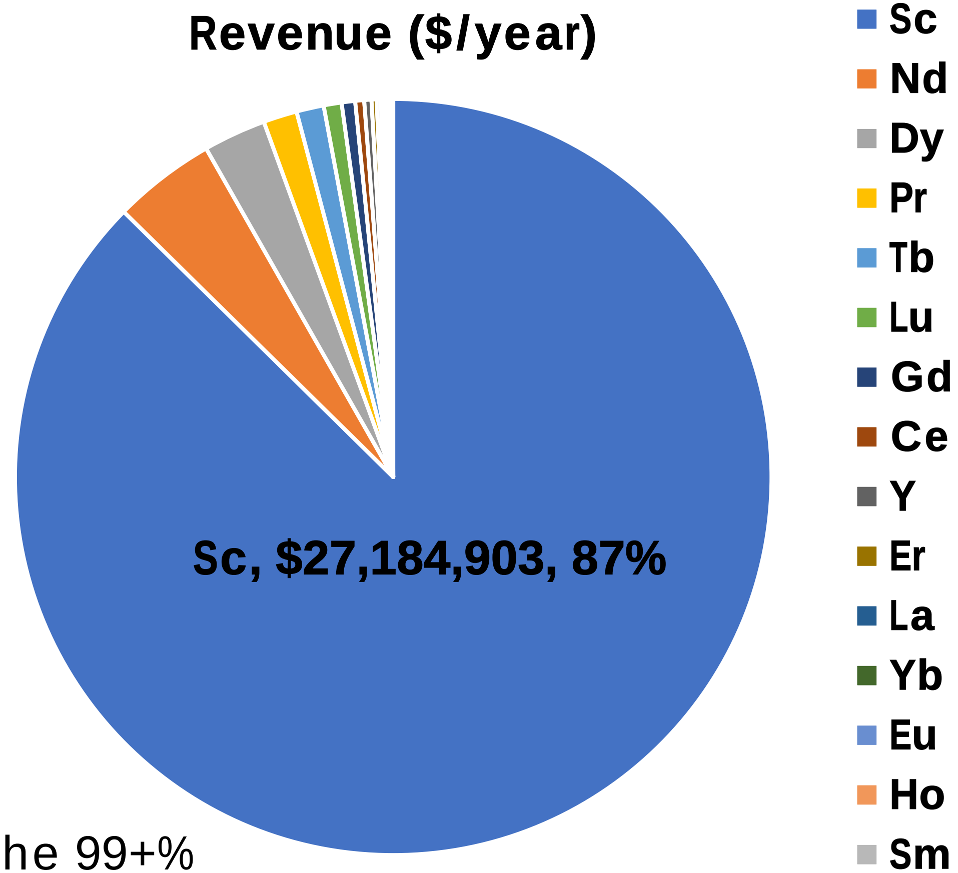
## Techno-economic analysis – process flow diagram



# Project Update

## Techno-economic analysis – revenue breakdown

| Plant operation assumptions **(500k tons/year of fly ash)** | |
|---|---|
| **Debt/equity (Capital)** | **60/40** |
| Term of debt financing | 10 years |
| Interest for debt financing | 8% per annum |
| **Plant Life** | **20 years** |
| Depreciation periods | 7, 15, 39 years |
| Income tax rate | 27% |
| **Start up time** | **6 months** |
| Operating time | 8000 hours/year |

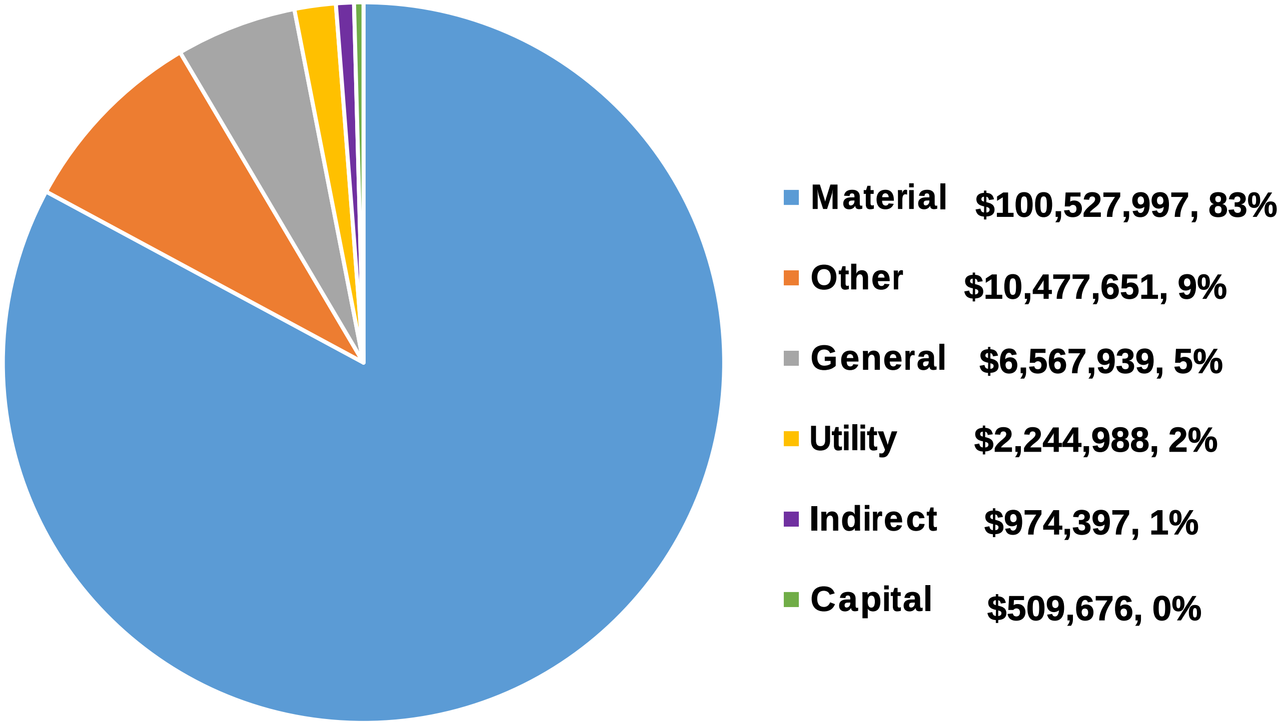



Our REO price was discounted by 30% from the 99+% pure individual REO prices quoted in 2018.

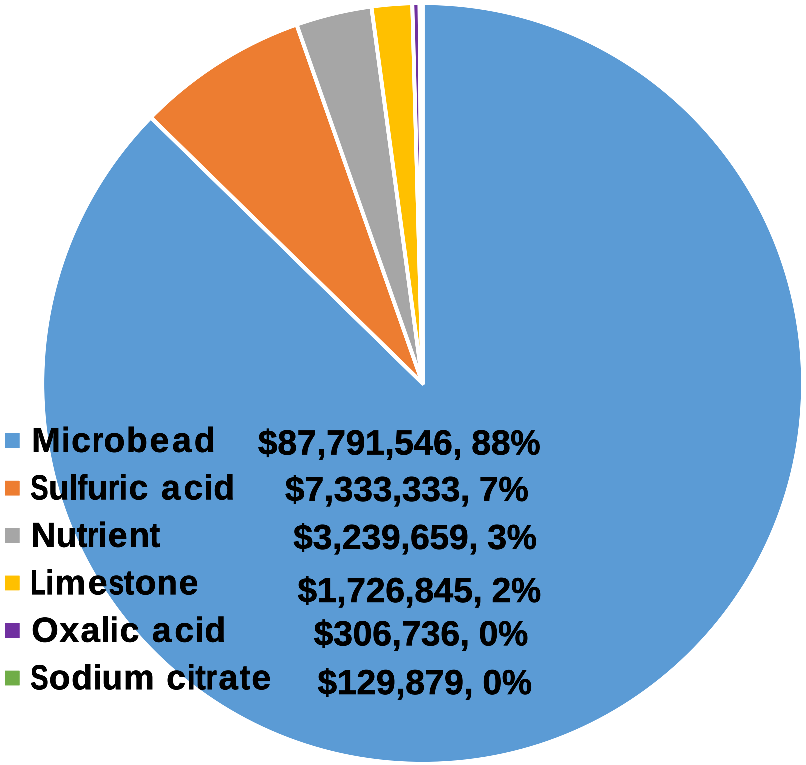
# Project Update

## Techno-economic analysis – cost breakdown

### Cost of processing 500k tons/year of APP fly ash ($/year)

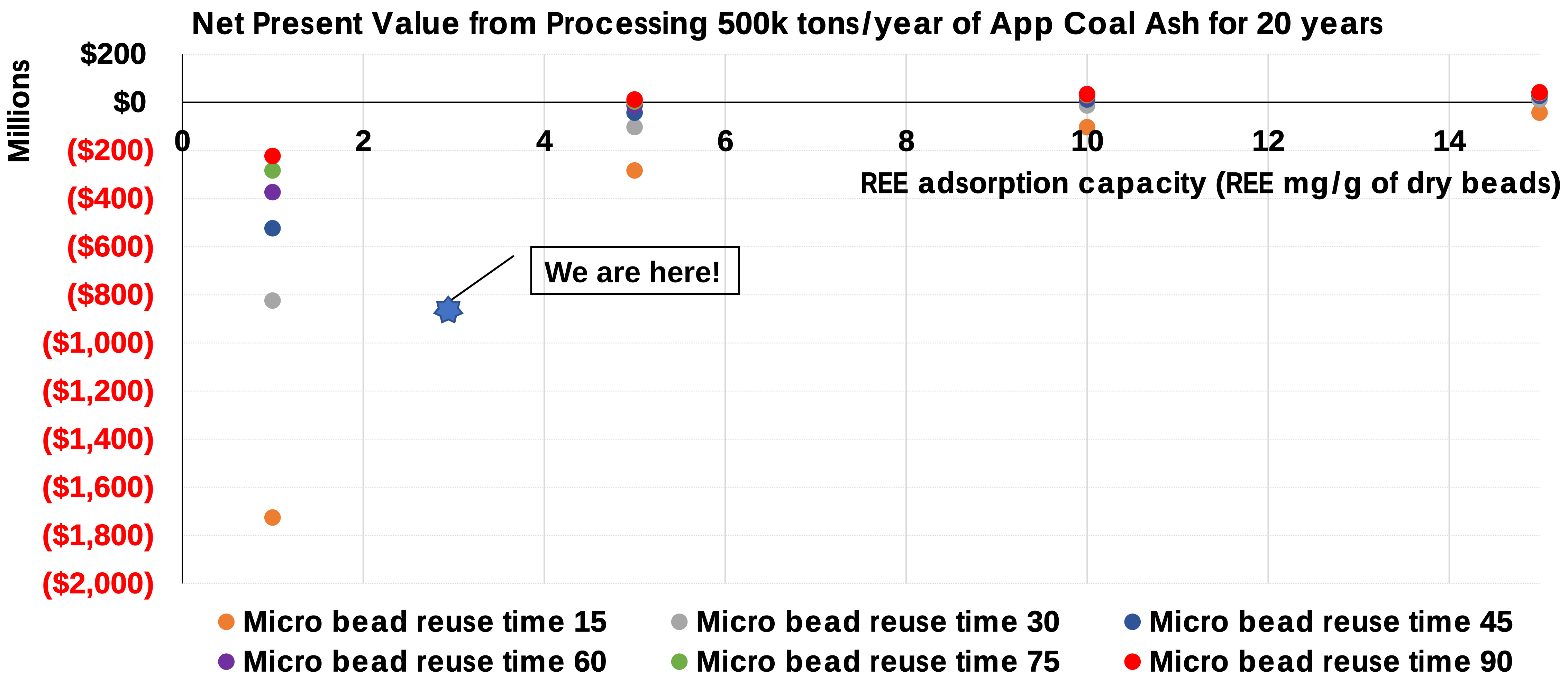



### Material cost breakdown ($/year)



# Project Update

## Techno-economic analysis – sensitivity analysis



# Preparing Project for Next Steps

## Transitioning and scale-up into bench scale production

### Market Benefits

- Fill a technology gap by converting coal byproducts to REE concentrate intermediate that can be further refined by existing technologies
- Provide an environmental friendly alternative for REE recovery and refinement.

### Technology-to-Market Path

- Improve on economics and transition towards scale-up
  - Decrease cost of microbe bead synthesis
  - Increasing cell loading and adsorption capacity
  - Engage with partners to scale up microbe bead production
  - Integrate packed-bed bioreactors for pilot tests
- Potential industrial partners: Navajo Transitional Energy Company, Solvey, Innovation Metals Corporation, Thor ORE

# Concluding Remarks

## Develop biosorbent with high selectivity for REEs

- Provide an economical and environmental friendly option for enriching and concentrating REEs from coal byproducts
  - A US patent entitled “Engineered Microbes for Rare Earth Element Adsorption” has been issued.
  - Selective extraction of REE from both pre- and post- combustion feedstocks using a single adsorption/desorption cycle.
- Next steps for tech development
  - Achieve an extraction efficiency of >80% and total REE purity >20 wt% from pre- and post- combustion coal byproducts.
  - Improve Sc recovery with leachate at pH 4
  - Transitioning and scaling to bench scale production

# Acknowledgements

NATIONAL ENERGY TECHNOLOGY LABORATORY

## Collaboration among LLNL, Duke U. and U. of Arizona

Dan Park

Co-PI

Helen Hsu-Kim

Hongyue Jin

Duke UNIVERSITY

THE UNIVERSITY OF ARIZONA

UND

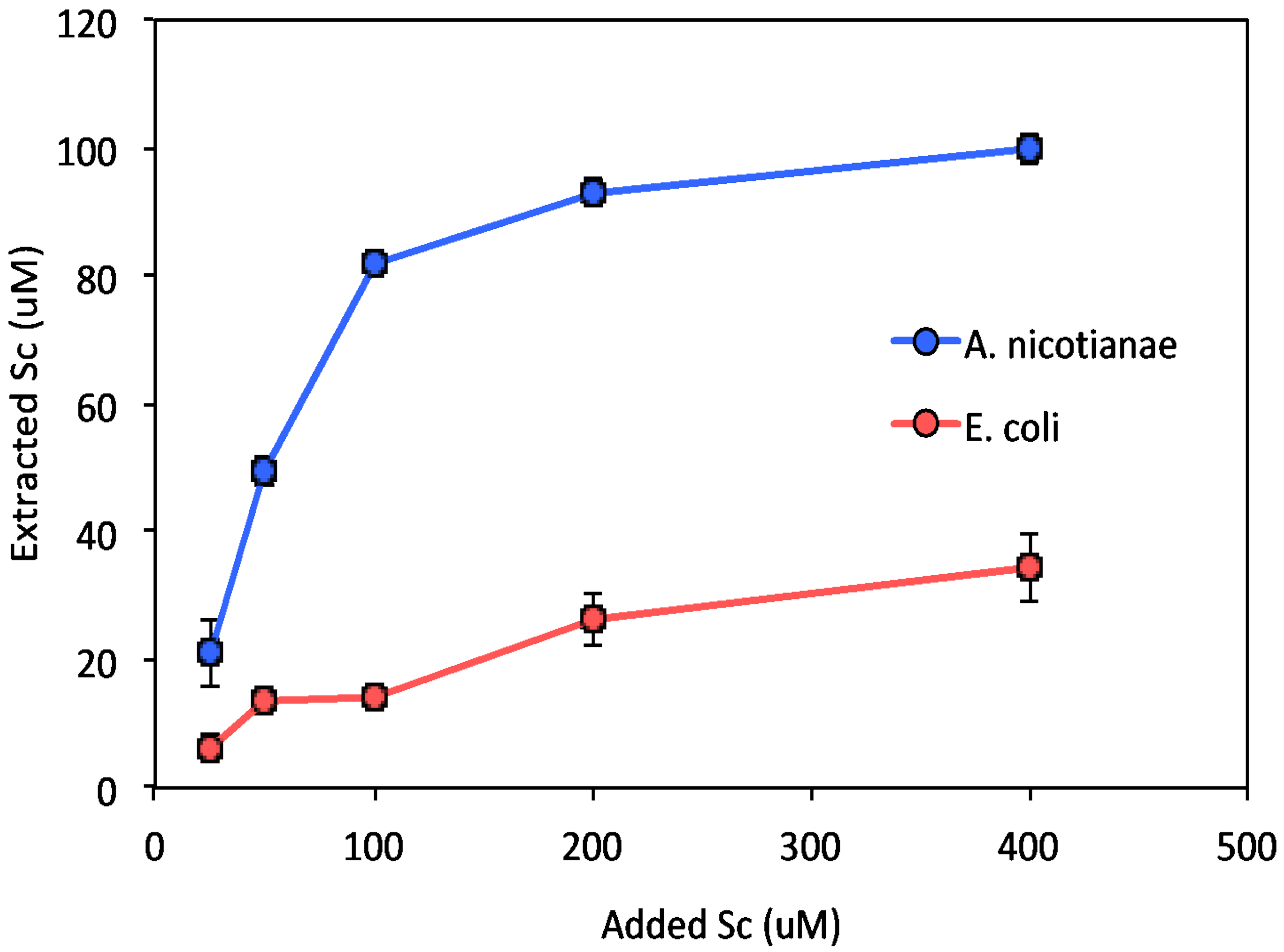
Navajo Transitional Energy Company

EMSL

SCIENTIFIC INNOVATION THROUGH INTEGRATION

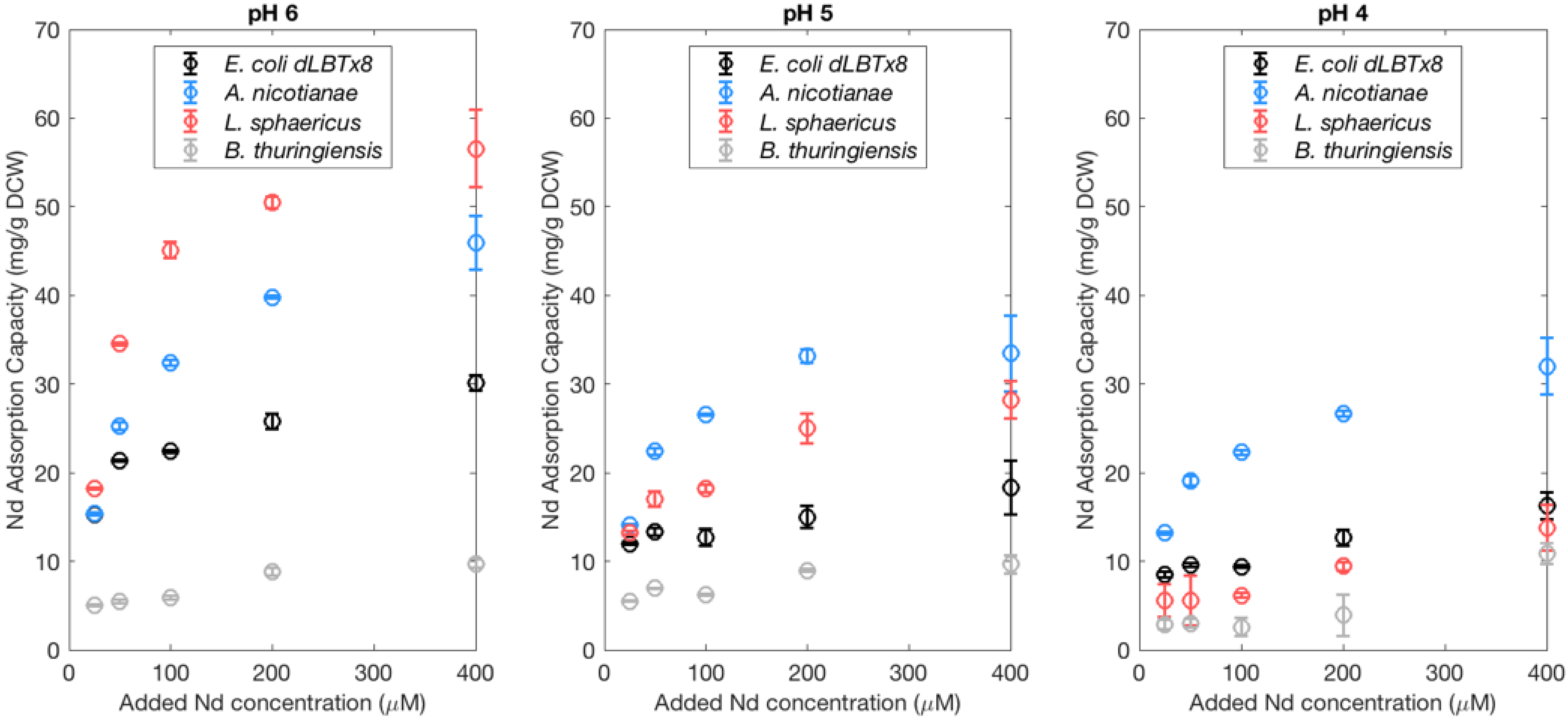
# Project Update

## Sc recovery from leachate of lignite at pH 4



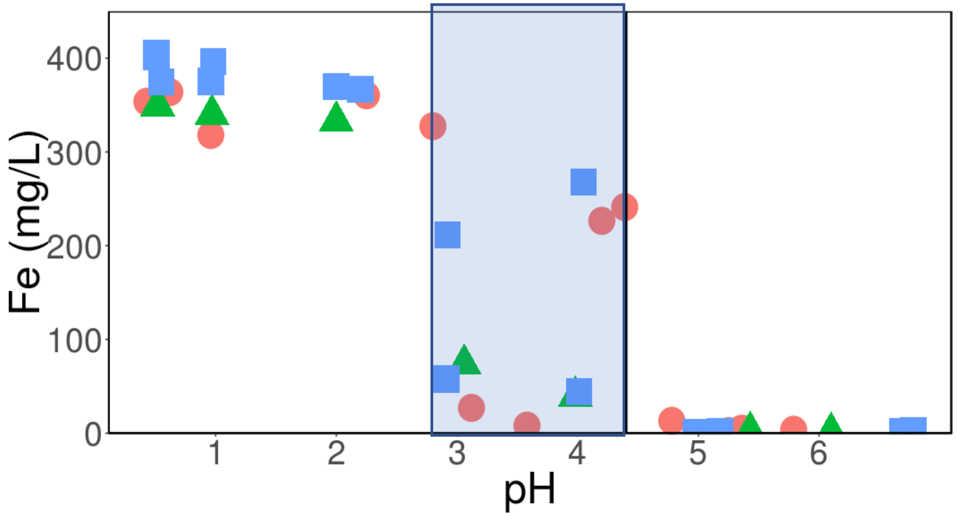
# Preparing Project for Next Steps

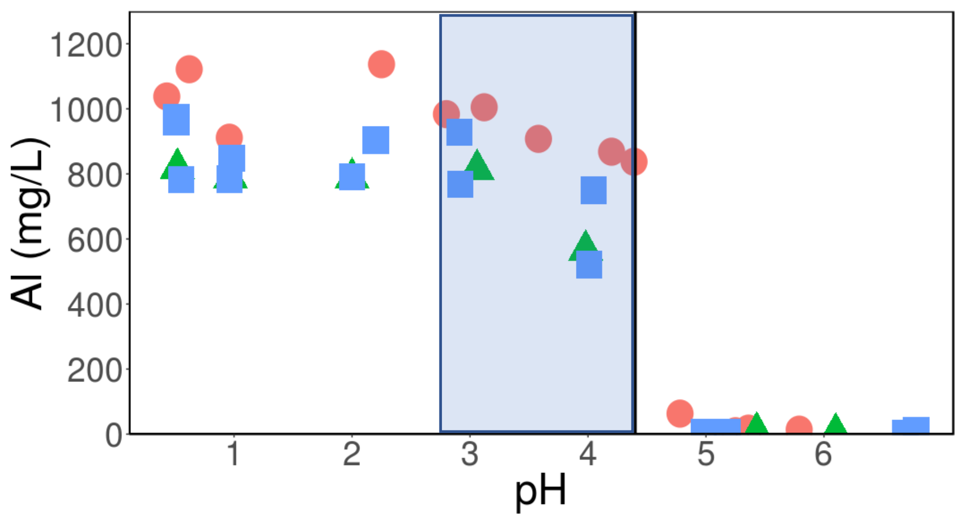
## Improve adsorption capacity at pH 4

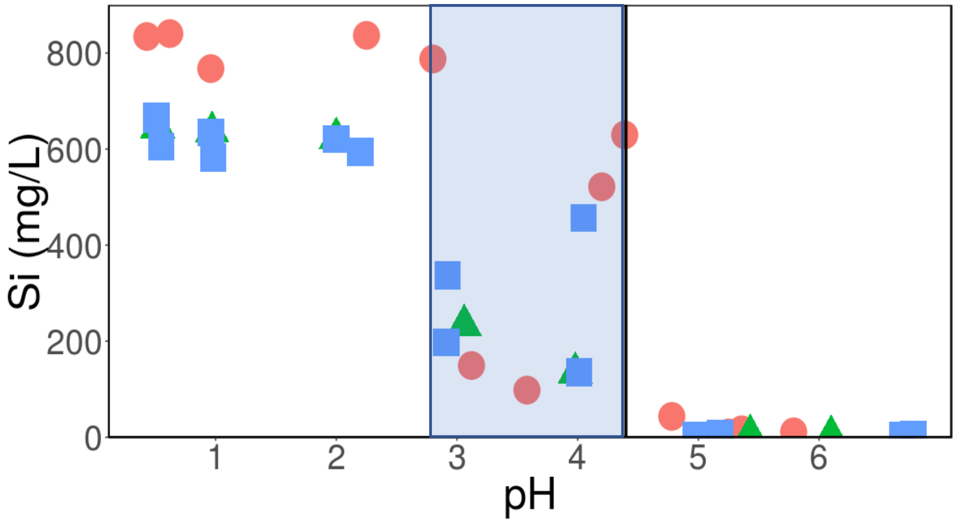


# Project Update

## PRB metal solubility of leachate upon pH adjustment

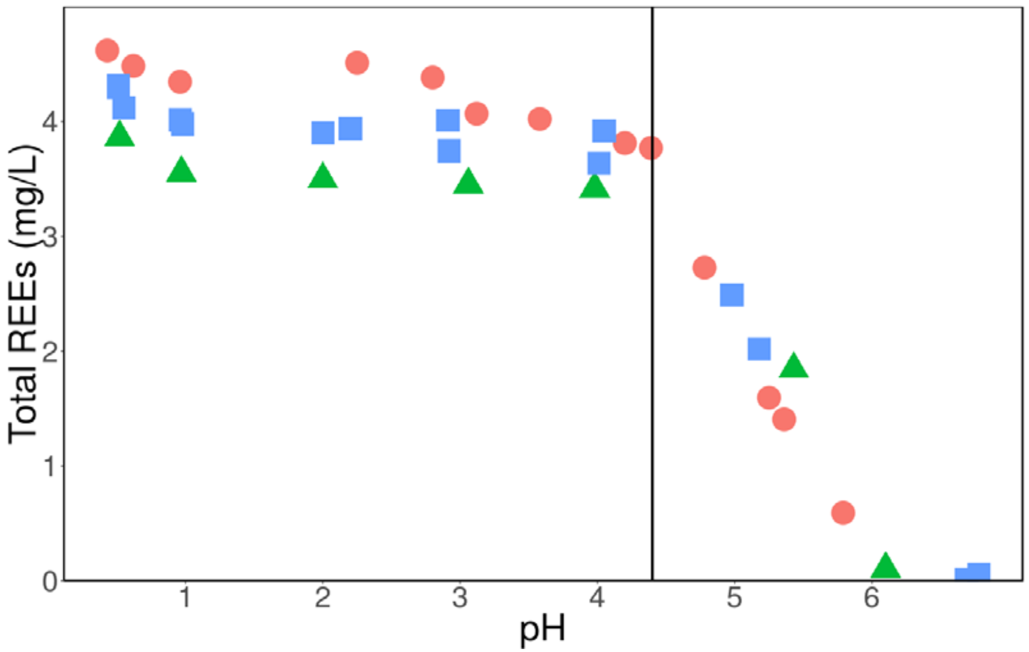


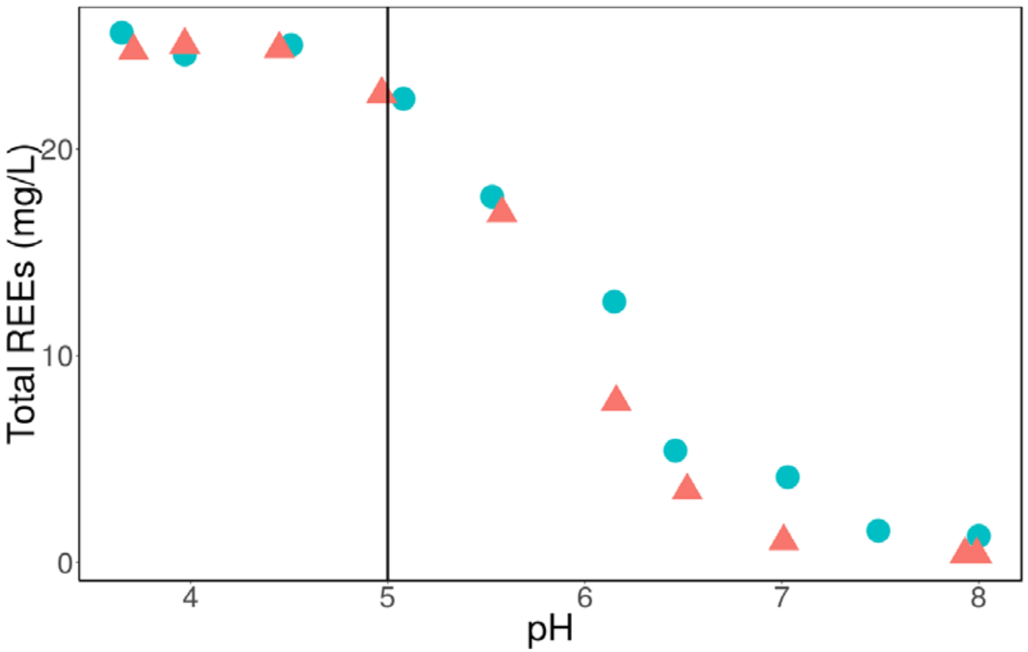



# Project Update

## REE solubility of PRB leachate upon pH adjustment




10 g/L ash

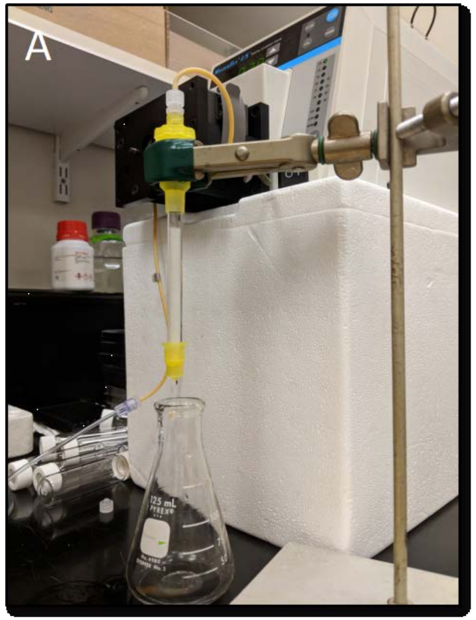


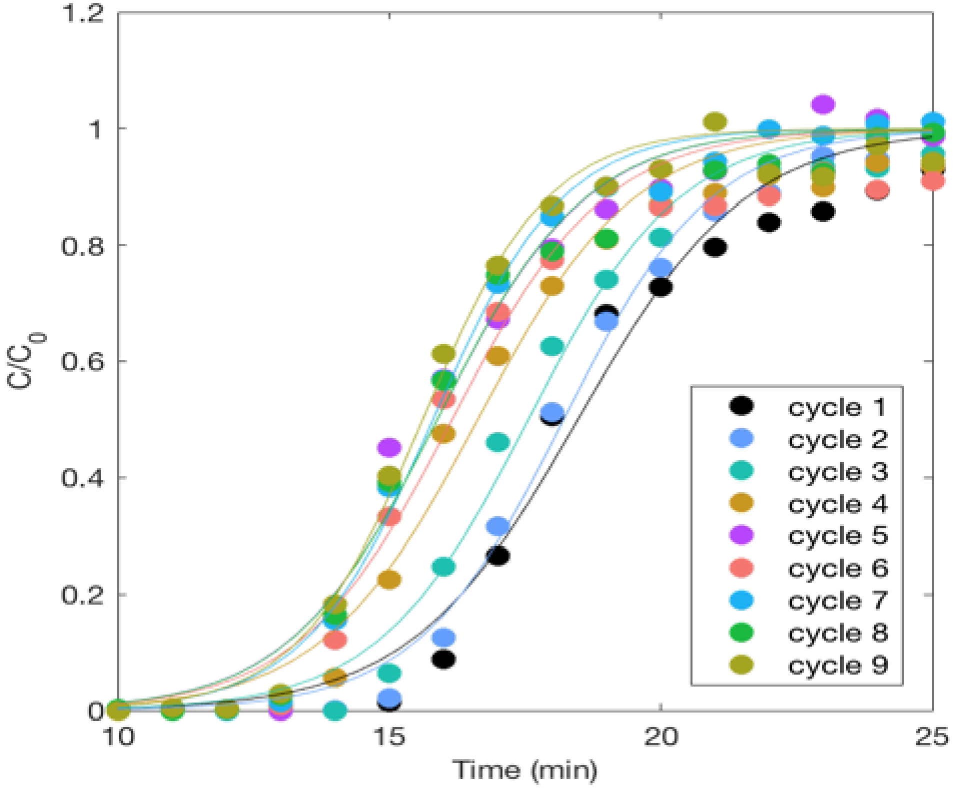

100 g/L ash

Profile of REE solubility over pH is affected by initial ash concentration.

# Project Update

## Column can be reused for multiple times




85% adsorption capacity was retained after 9 adsorption/desorption cycles.

Aaron Brewer, unpublished

# Project Update

## Bioengineered microbes exhibit high selectivity for REEs of high criticality

Surface displayed LBTs are specific for REE metal ions

| REE | $K_D$ (μM) |
|---|---|
| **$Tb^{3+}$** | **3.8 (0.3)** |
| $Al^{3+}$ | 320 (80) |
| $Fe^{3+}$ | 210 (0.7) |
| $Co^{2+}$ | 976 (48) |
| $Mn^{2+}$, $Ni^{2+}$ | >4000 |
| $Mg^{2+}$, $Zn^{2+}$, $Ca^{2+}$ | >>10,000 |
| $Cu^{2+}$* | >300 |

Surface displayed LBTs preferentially bind REEs with smaller atomic radii

| REE | $K_D$ (μM) |
|---|---|
| Eu* | 2.5 (0.2) |
| Yb | 3.1 (0.3) |
| Dy* | 3.2 (0.7) |
| Tb* | 3.8 (0.3) |
| Y* | 5.7 (0.1) |
| Nd* | 13.3 (3.8) |
| Ce | 114 (53) |
| La | 153 (55) |